

Calorimetry and scanning thermal measurements

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Ames Laboratory

And

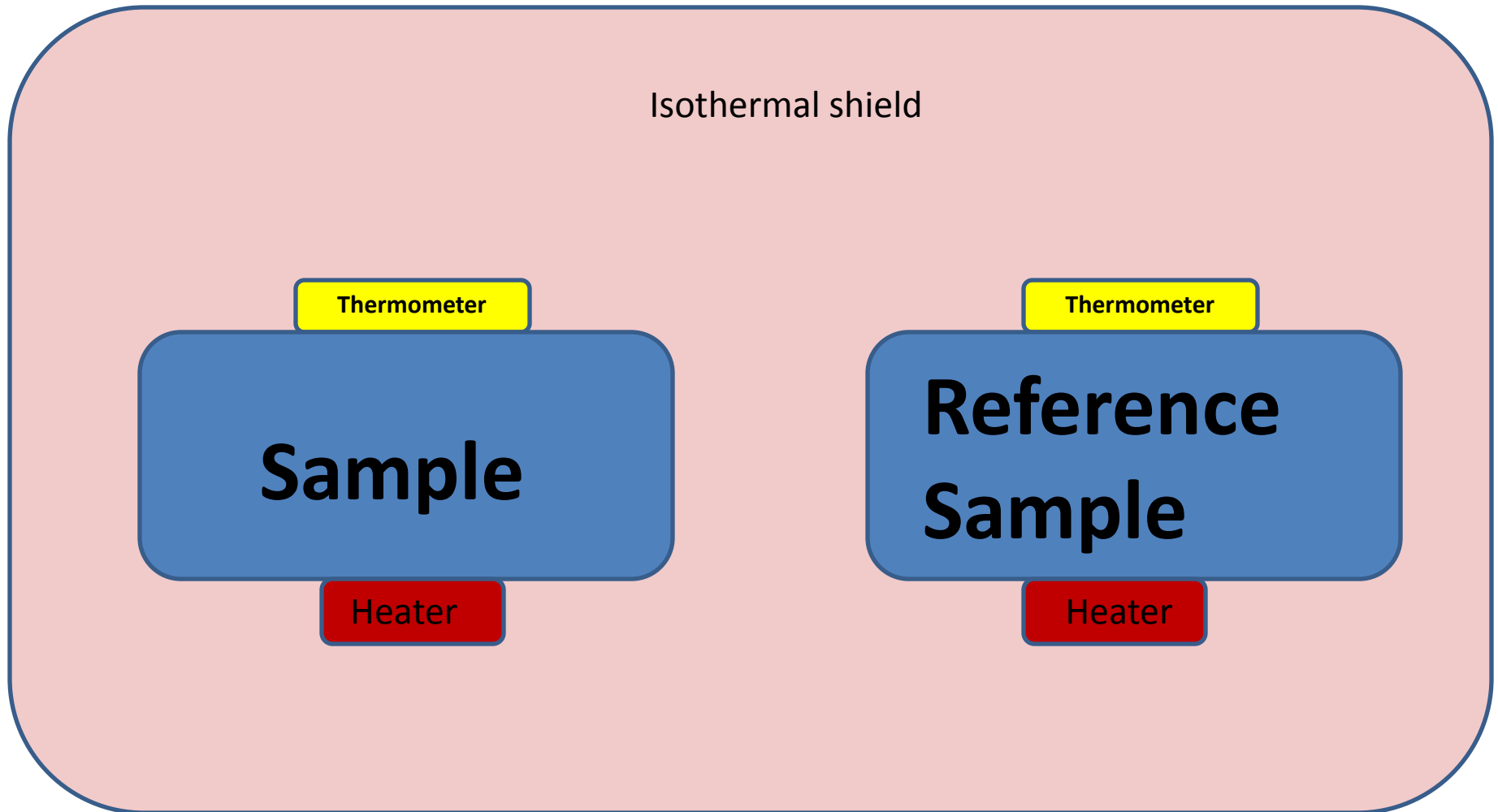
Materials Science and Engineering

Types of thermal analysis

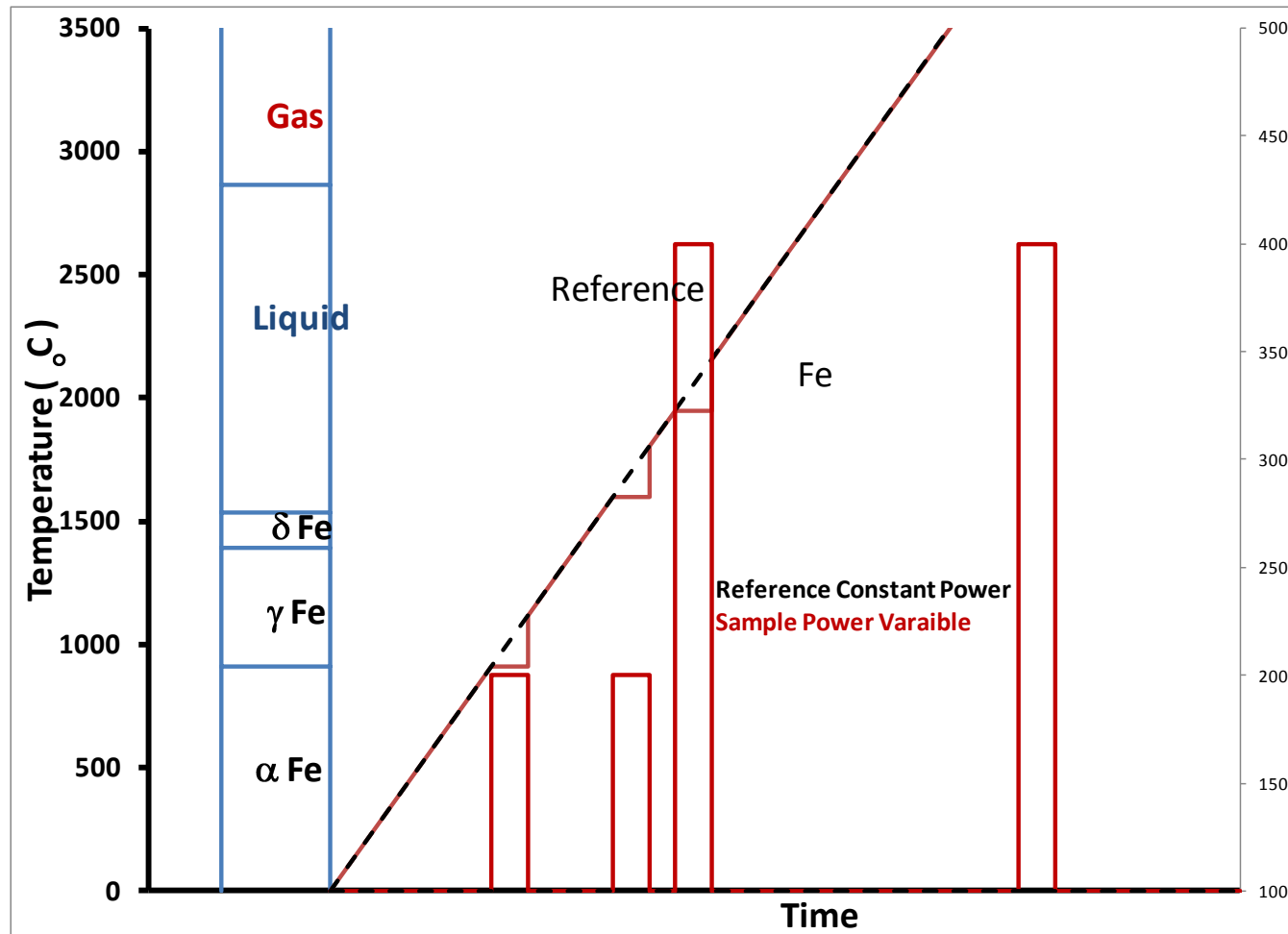
- Semi Adiabatic Specific Heat
- **DTA** differential thermal analysis (rt to 1650 °C)
- **DSC** Differential Scanning Calorimetry (rt to 750 °C)
- **Heat flux DSC** (rt to 1650 °C), (-150 to 900 °C)
- **TGA** thermal gravimetric analysis (rt – 1500 °C)
- **STA** simultaneous thermal analysis (rt – 1500 °C)
- **TMA**
 - thermo mechanical analysis
 - Thermo magnetic analysis
- Dilatometry (thermal expansion)
 - (rt to 1650 °C), (-150 to 900 °C)

Differential Calorimeter

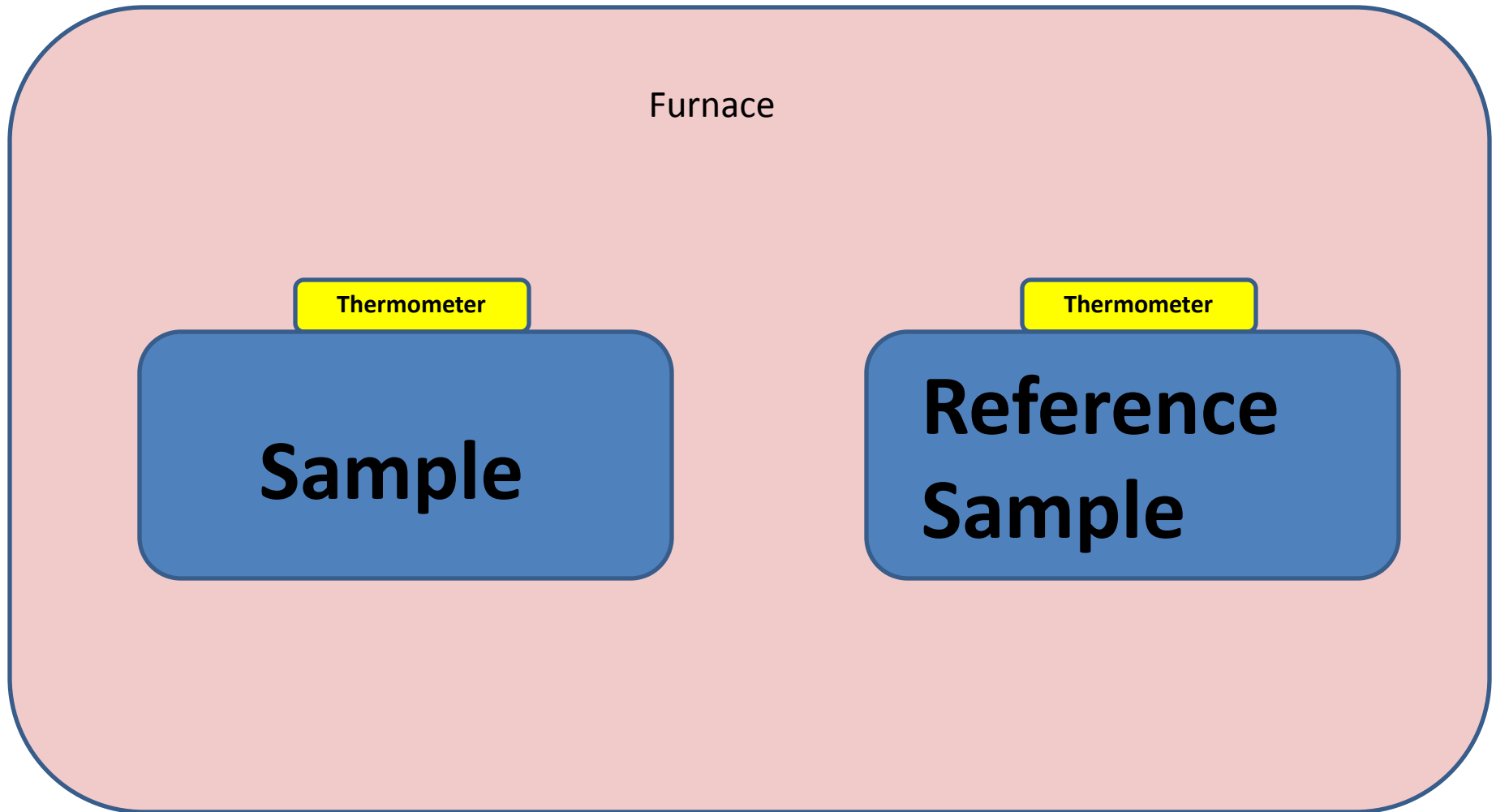
heater power adjusted for equal temperature both samples
(power compensated)



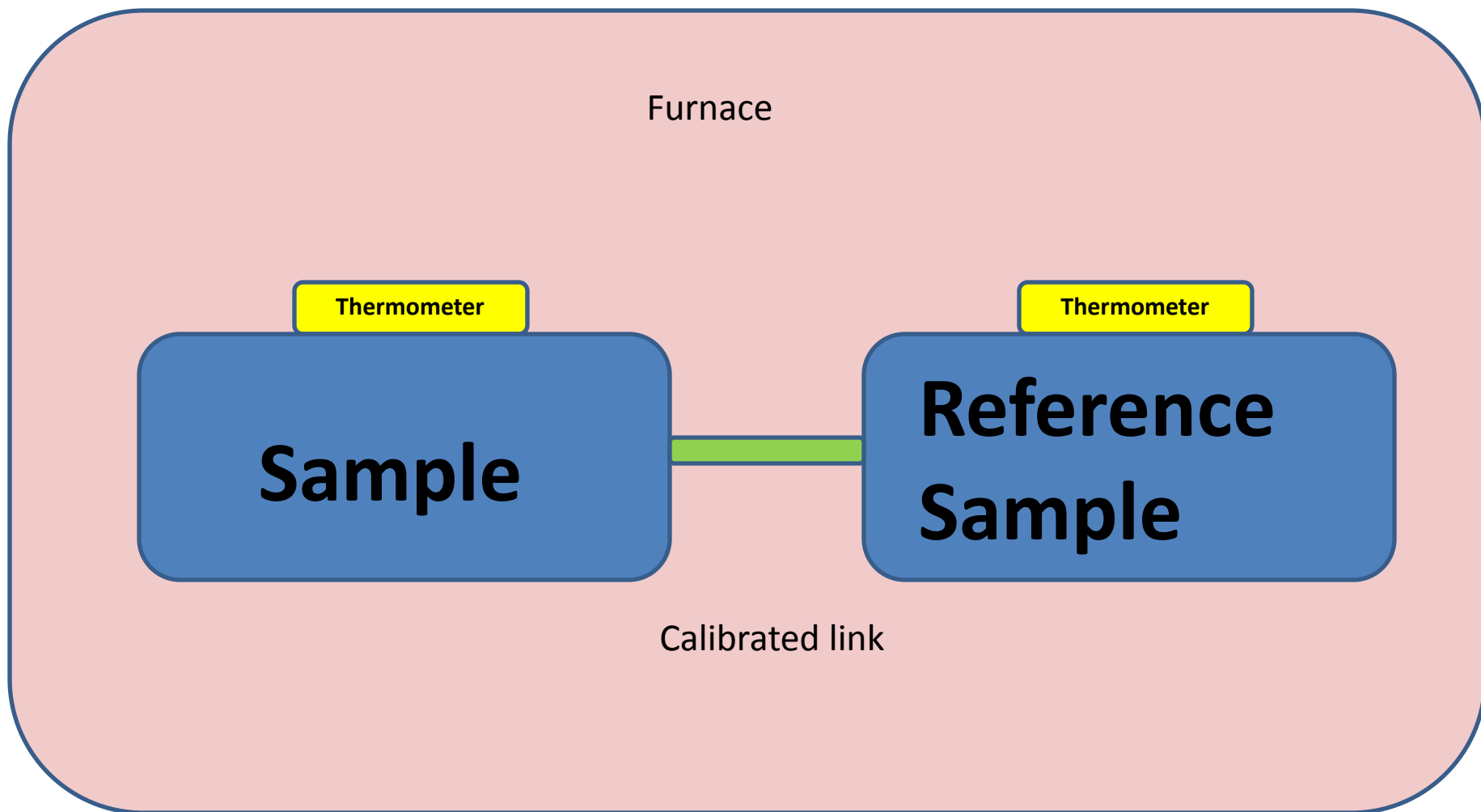
DSC



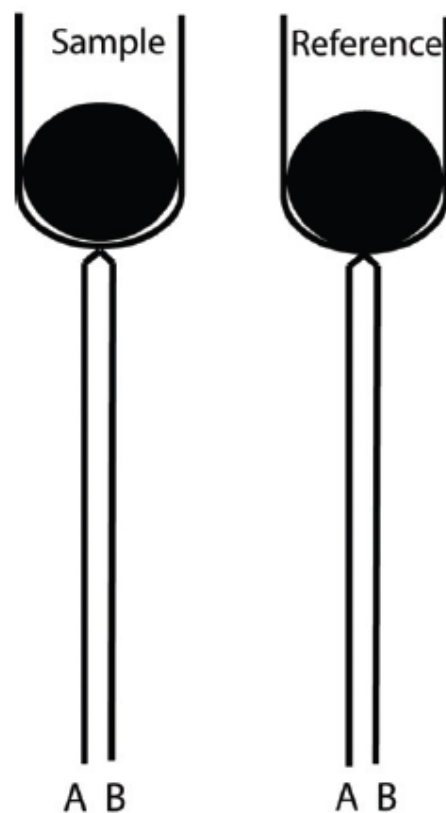
Differential Thermal Analysis



Differential Heat Flux Calorimeter



DTA



Heat Flux DSC

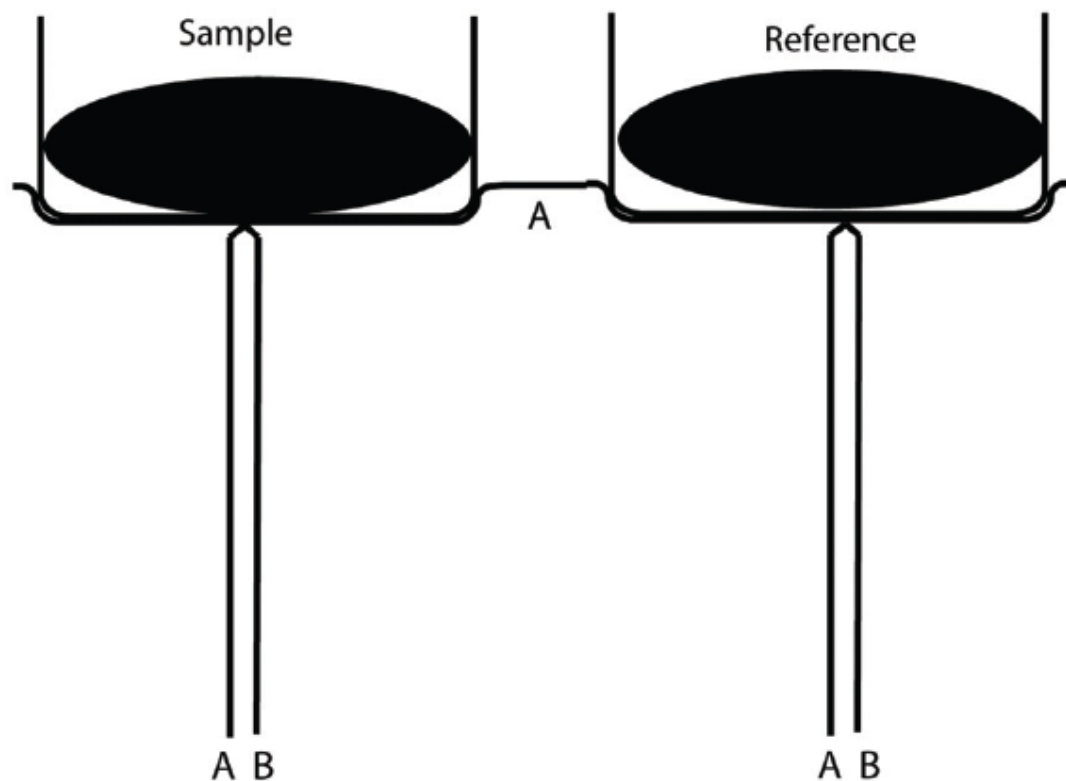


Figure 2.1. Schematic of DTA and HF-DSC geometries (not to scale). *A* and *B* denote the different legs of thermocouples.

Melting curve

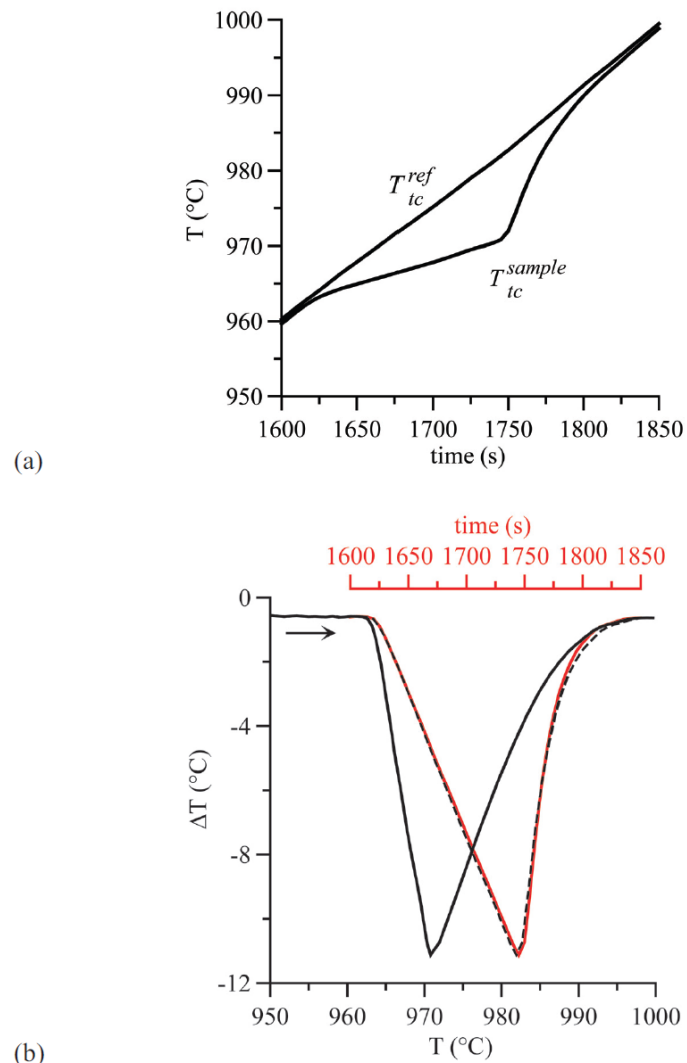
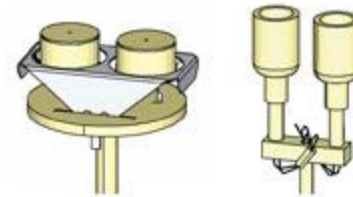


Figure 2.2. DTA melting of a 211.6 mg of pure Ag at 10 K/min. (a) Reference thermocouple temperature T_{tc}^{ref} and sample thermocouple temperature T_{tc}^{sample} vs. time. (b) Differential signal $\Delta T = T_{tc}^{sample} - T_{tc}^{ref}$ vs. time (red), vs. sample temperature (solid black), and vs. reference temperature (dashed black). For this data, the reference temperature remains quite linear in time as the sample melts, so that a linear scaling of the time axis makes the plots with x-axes of time and reference temperature practically identical.

Netzsch DSC 404 C Pegasus®



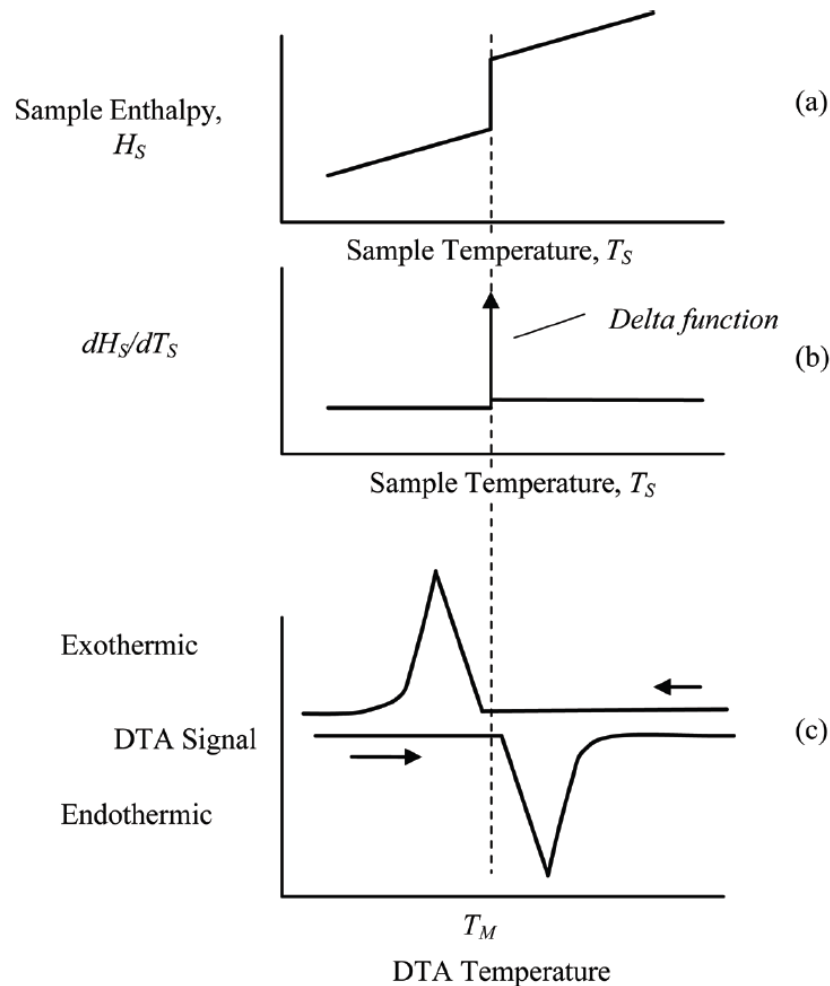


Figure 2.5. Schematic a) enthalpy vs. temperature for a pure metal; b) corresponding derivative $dH_S(T_S)/dT_S$ curve; c) DTA signal for melting (bottom) and freezing (top). The small difference in heat capacity of liquid and solid leads to a small offset of the baseline before and after melting. The onsets in the DTA curves are shown with a small deviation from the melting point, T_M , due to heat flow limitation in the DTA. This difference on melting is adjusted to zero by the calibration procedure, at least for one heating rate.

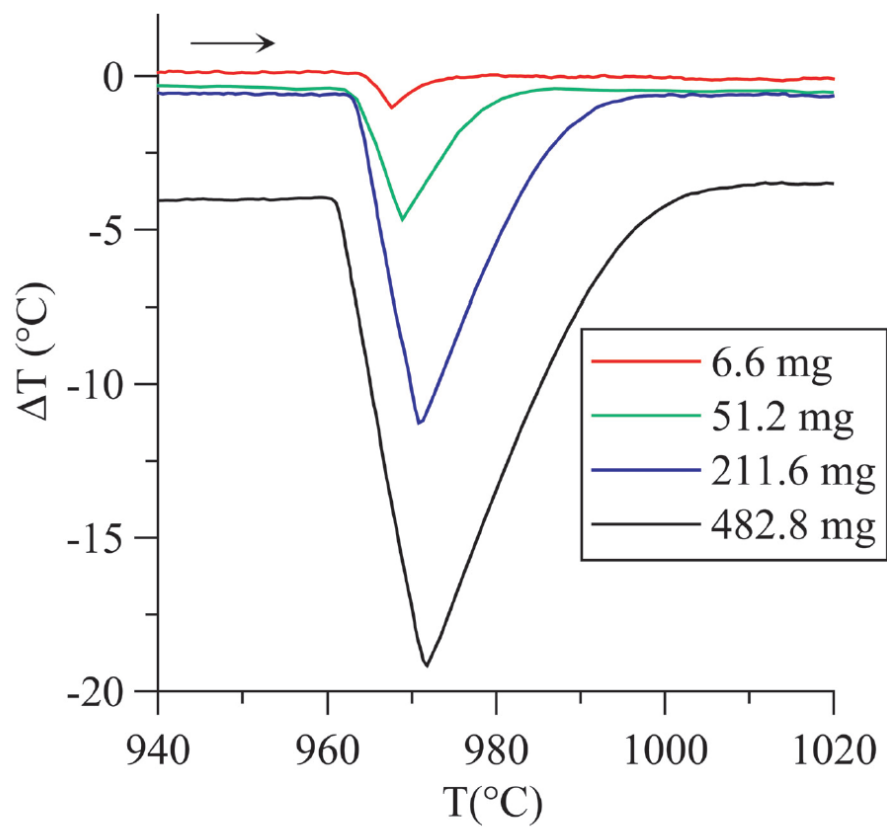
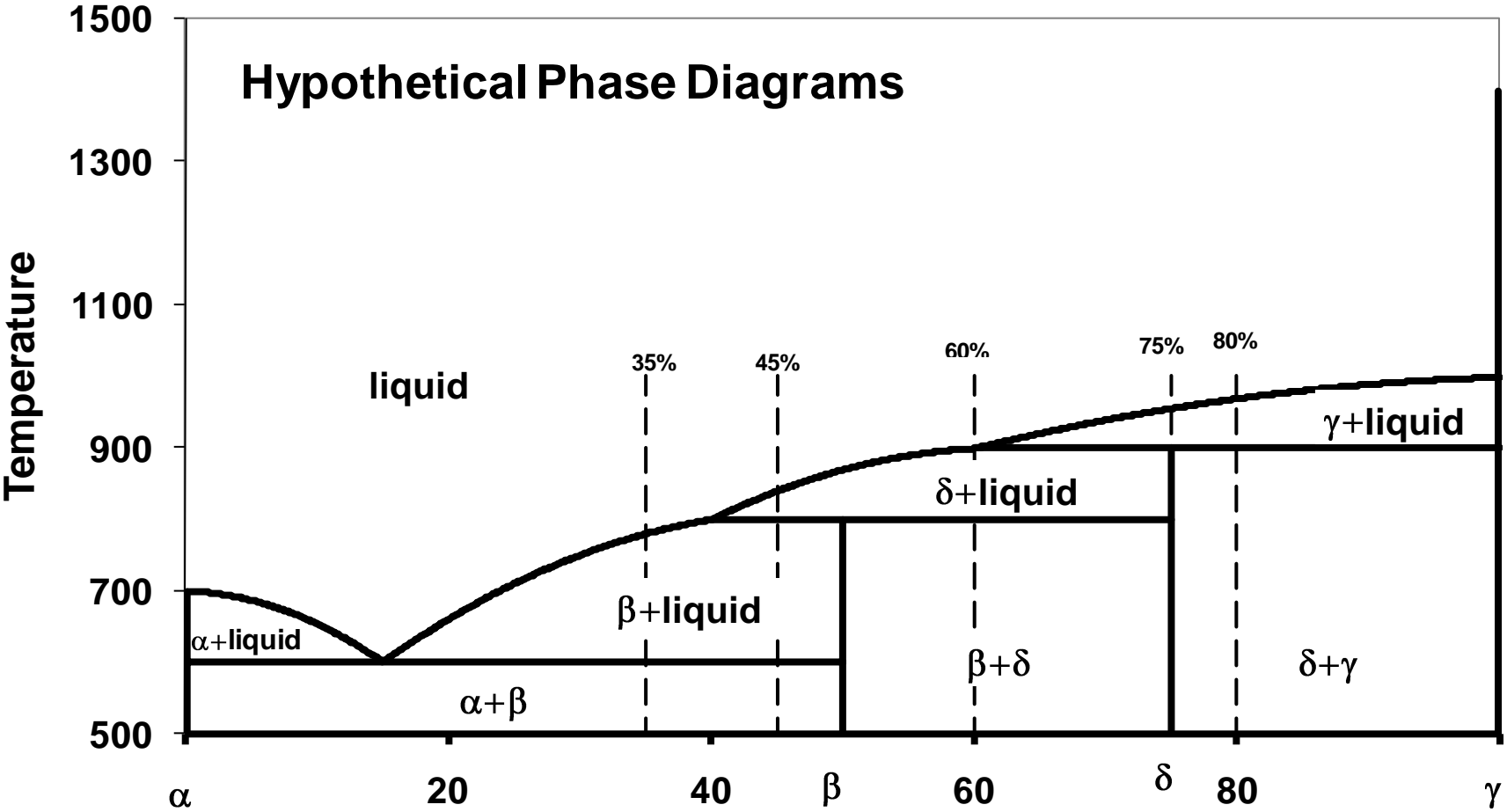
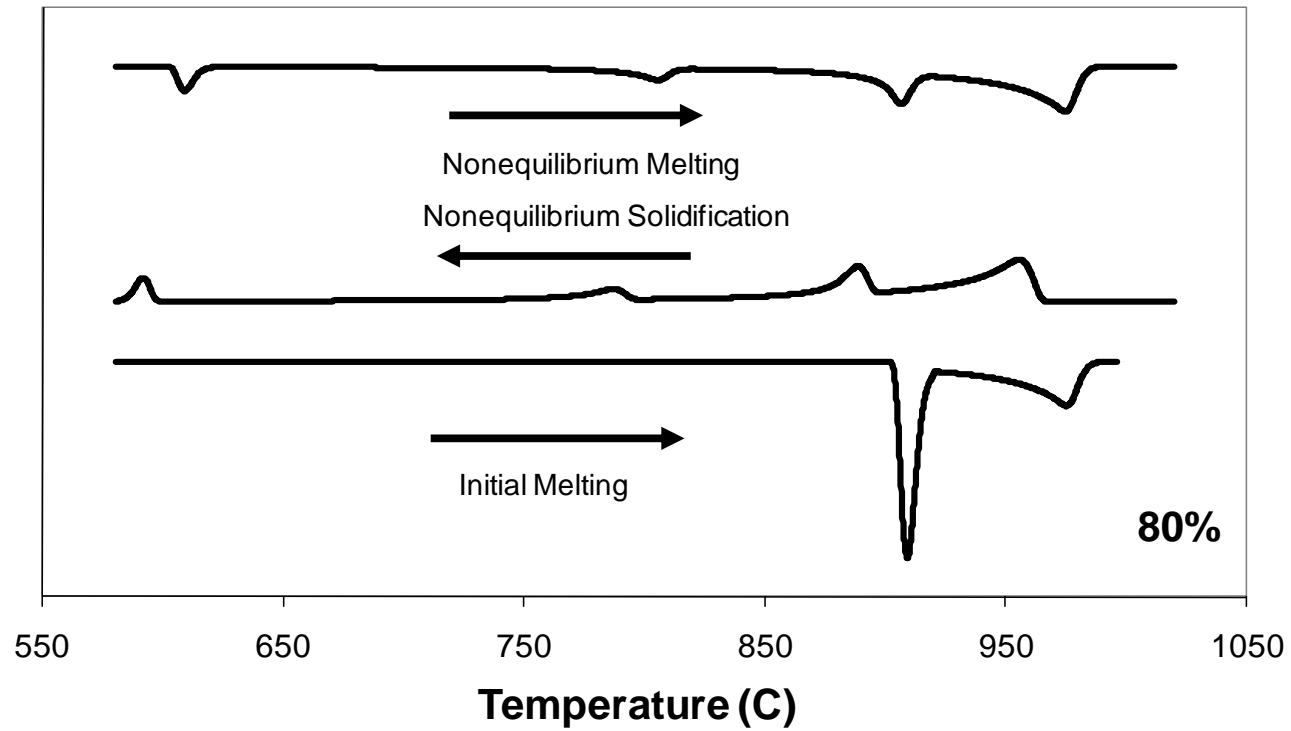
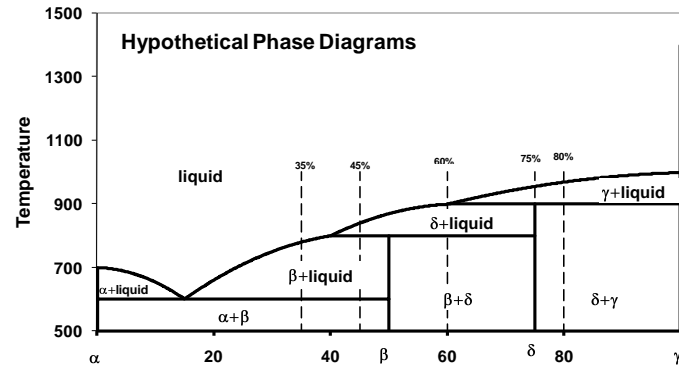
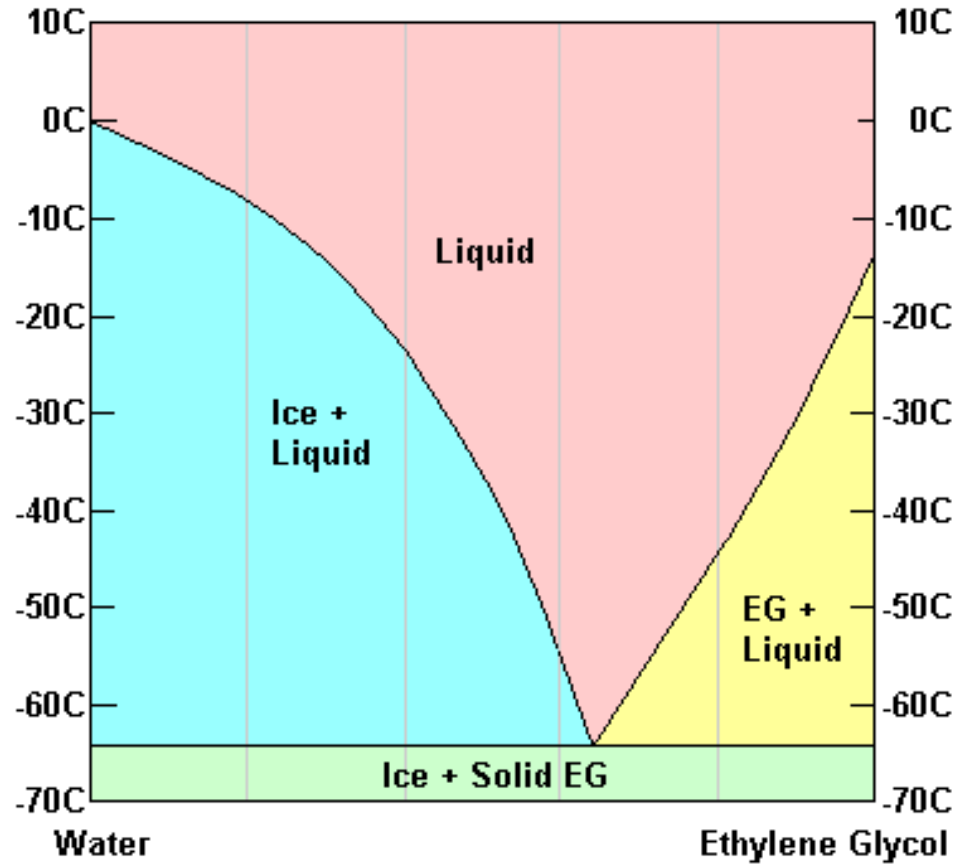


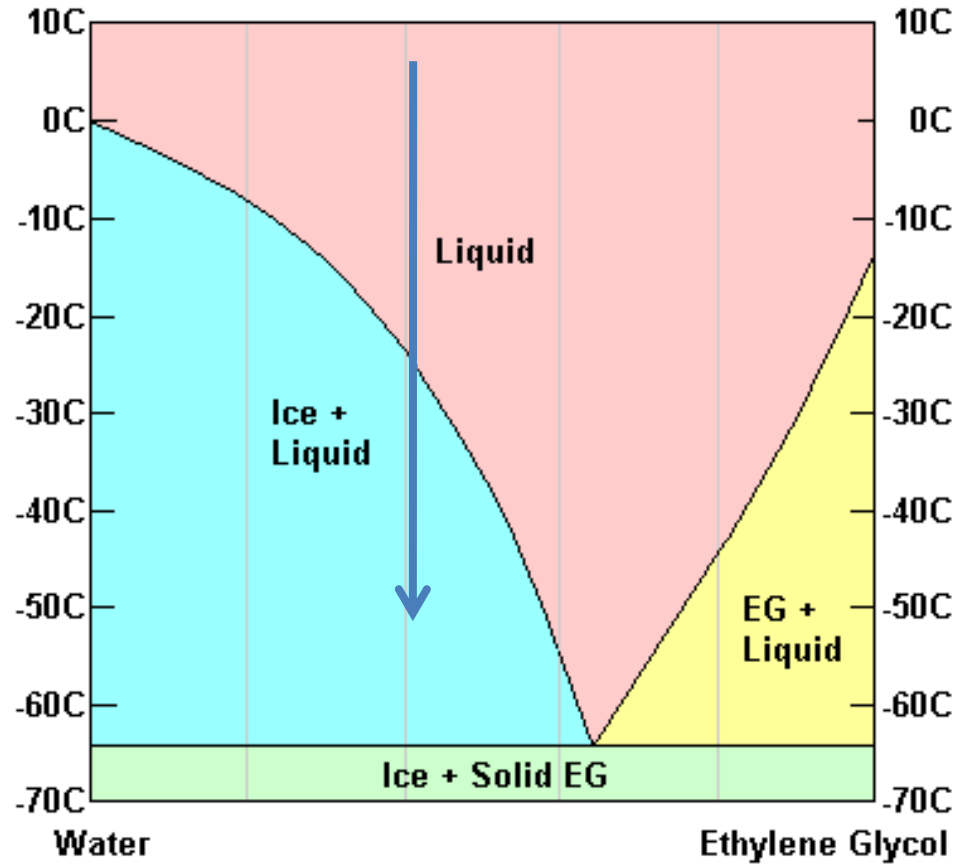
Figure 2.3. Effect of sample mass on DTA signal for pure Ag. The reference mass was held constant. Heating rate is 10 K/min.

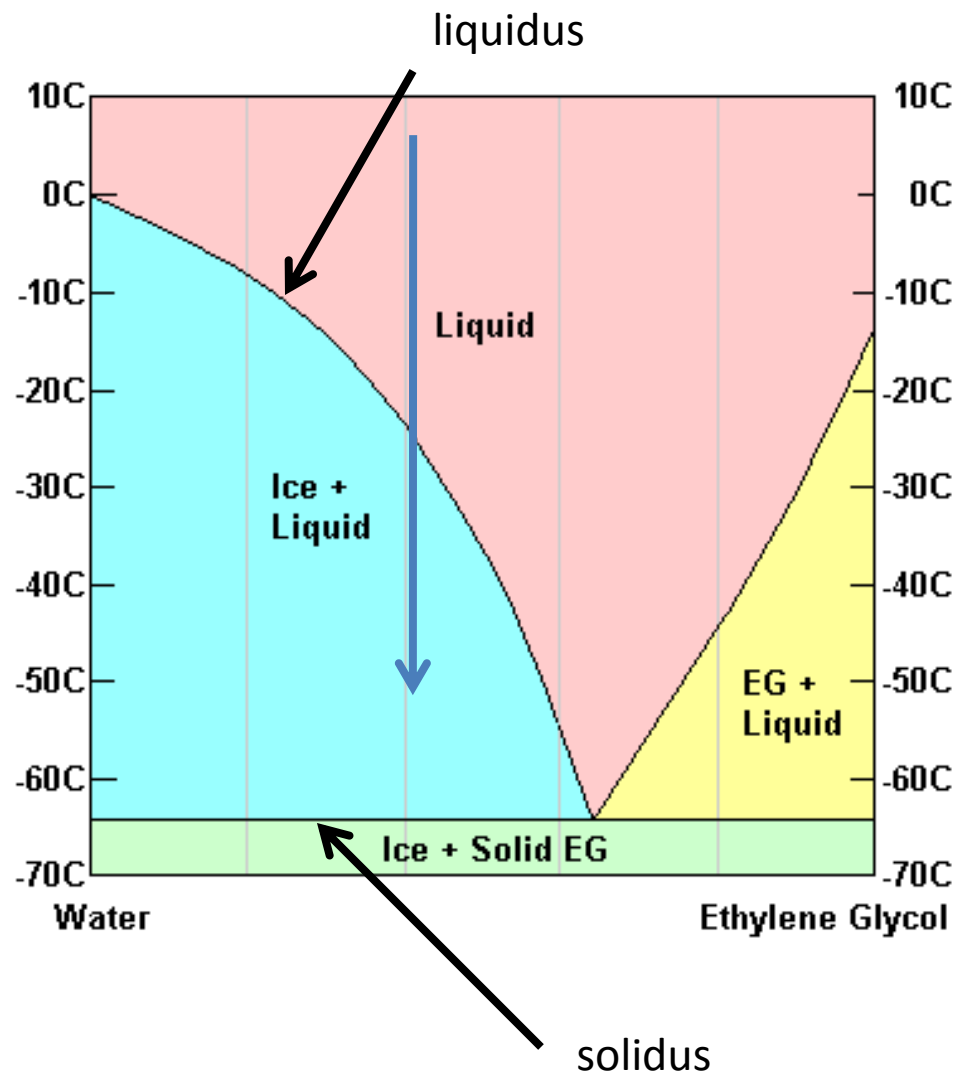
Hypothetical Phase Diagrams

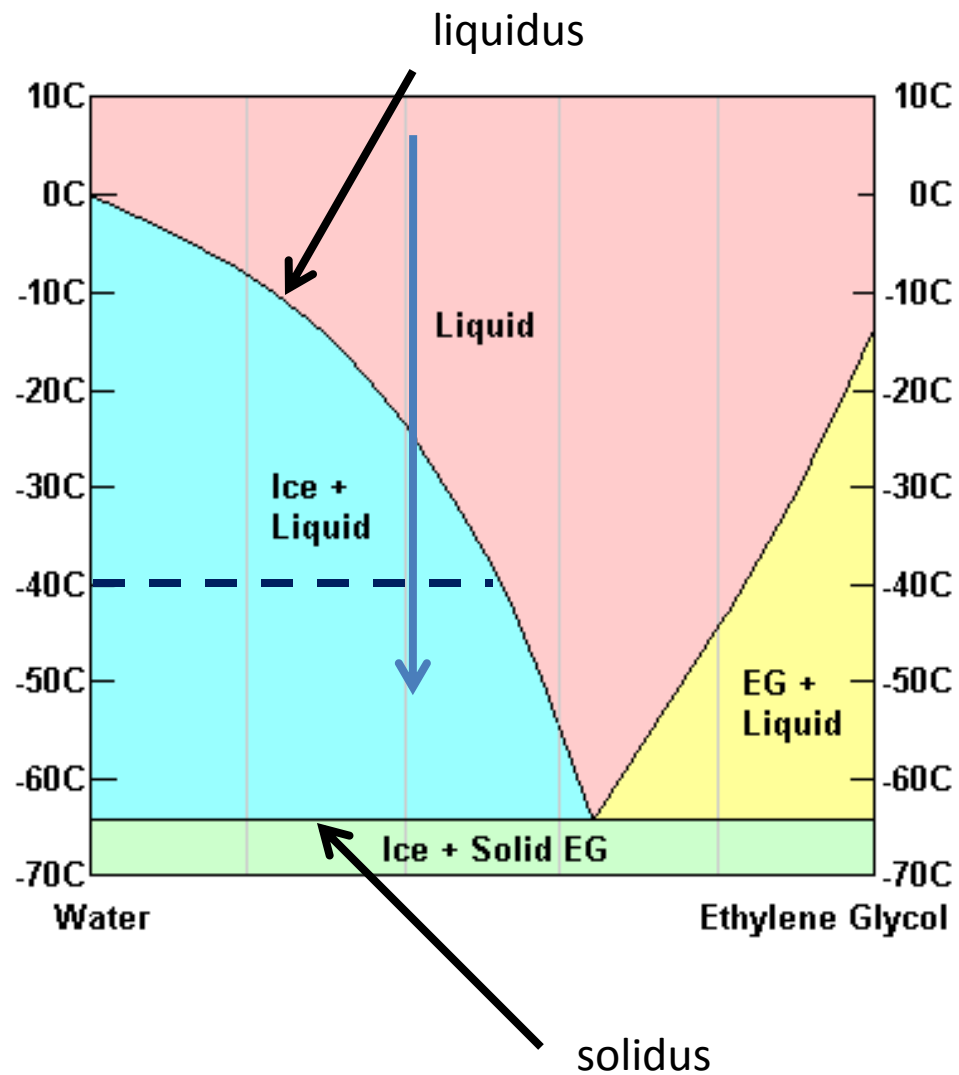


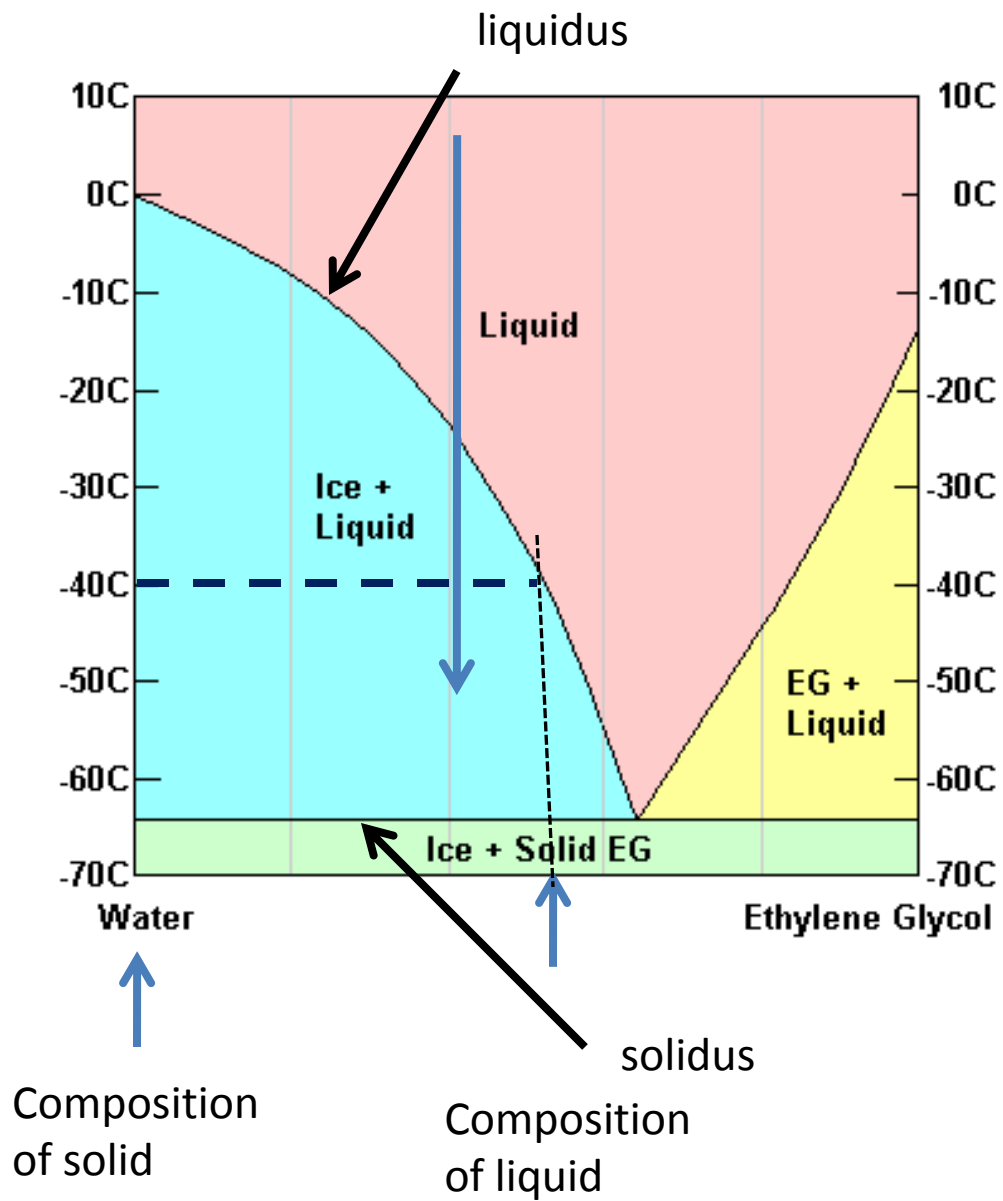


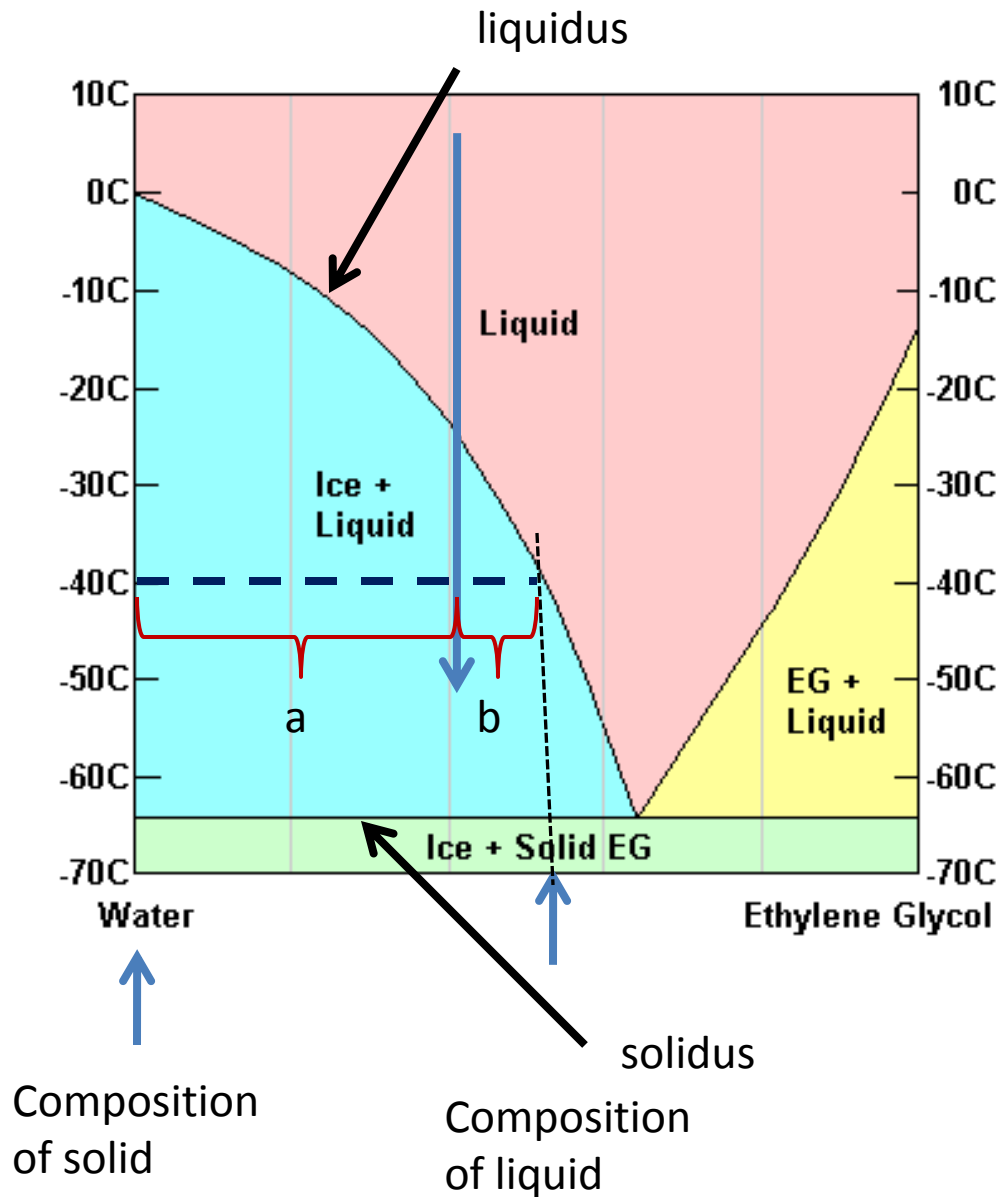






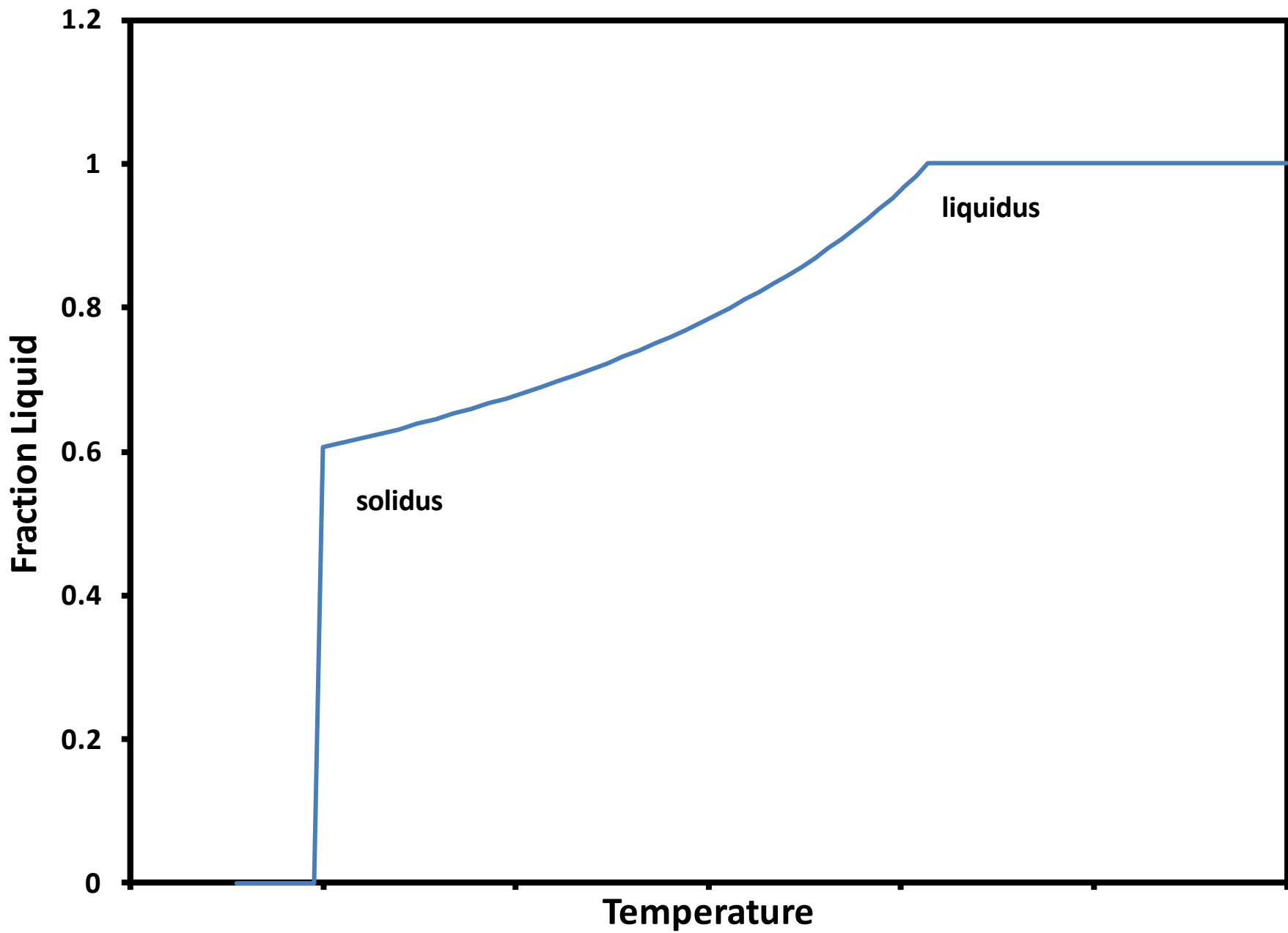


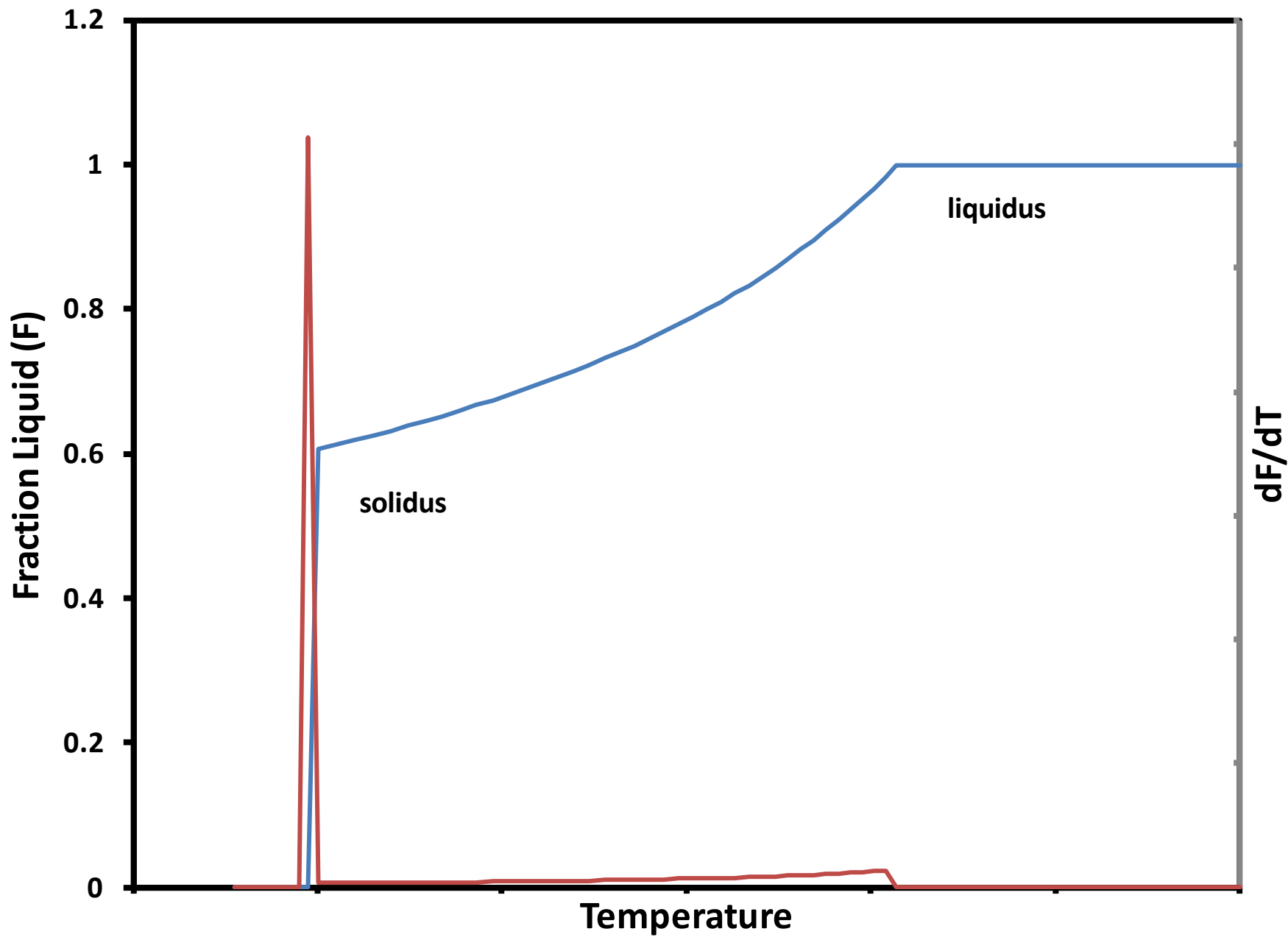


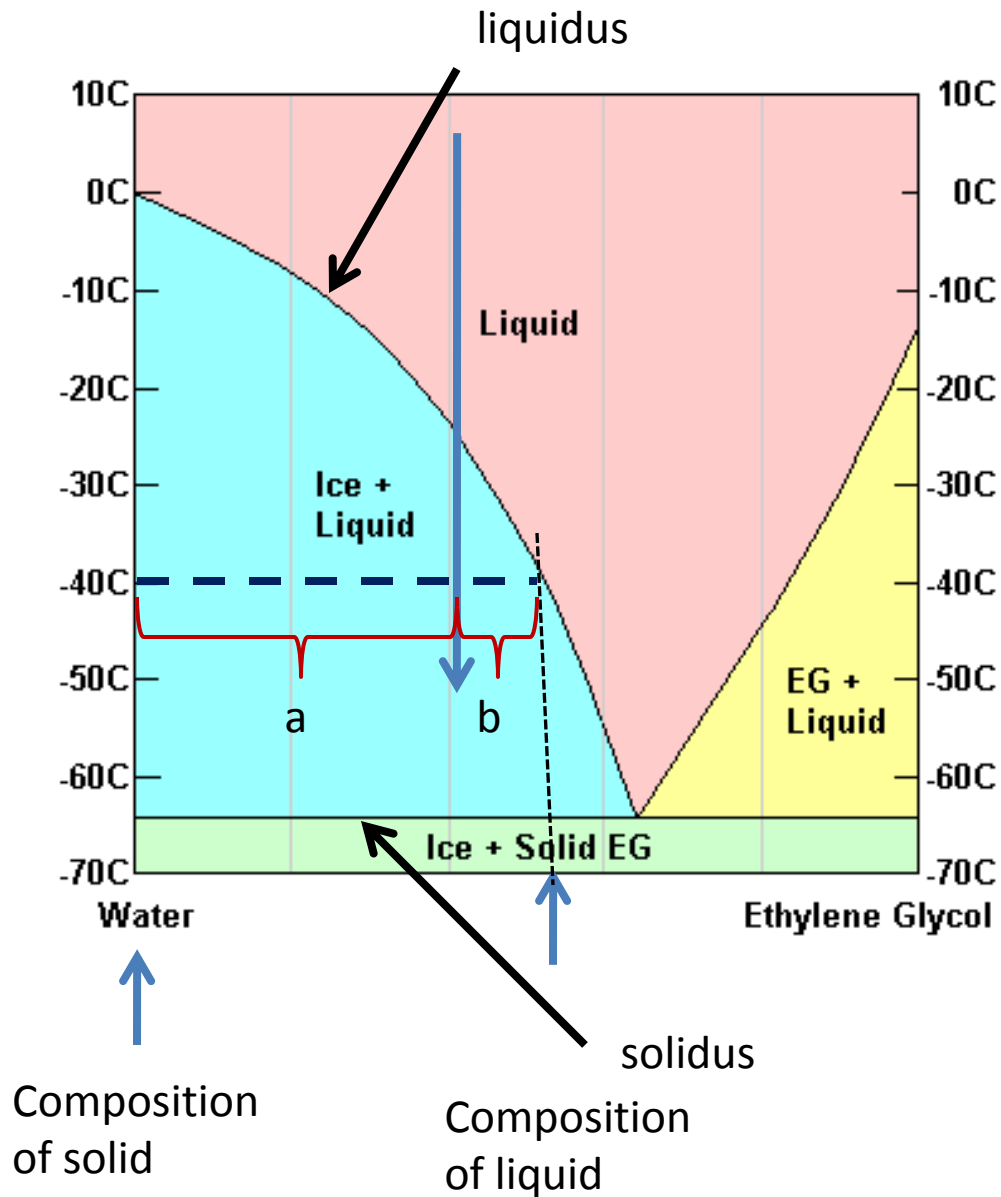


$$\text{Fraction of liquid} = \frac{a}{a+b}$$

$$\text{Fraction of solid} = \frac{b}{a+b}$$

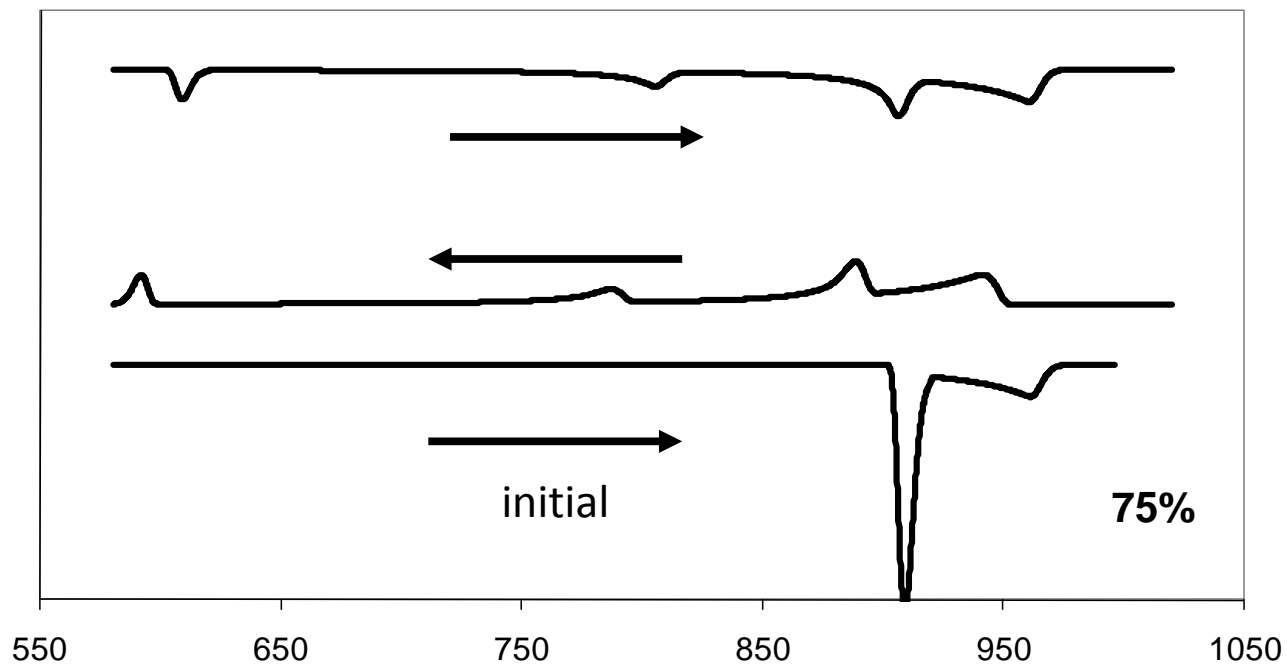
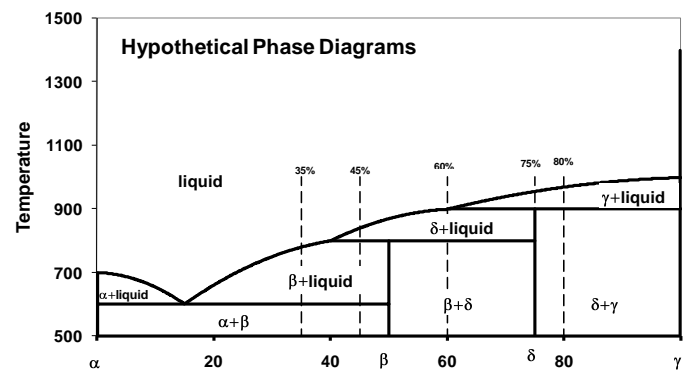


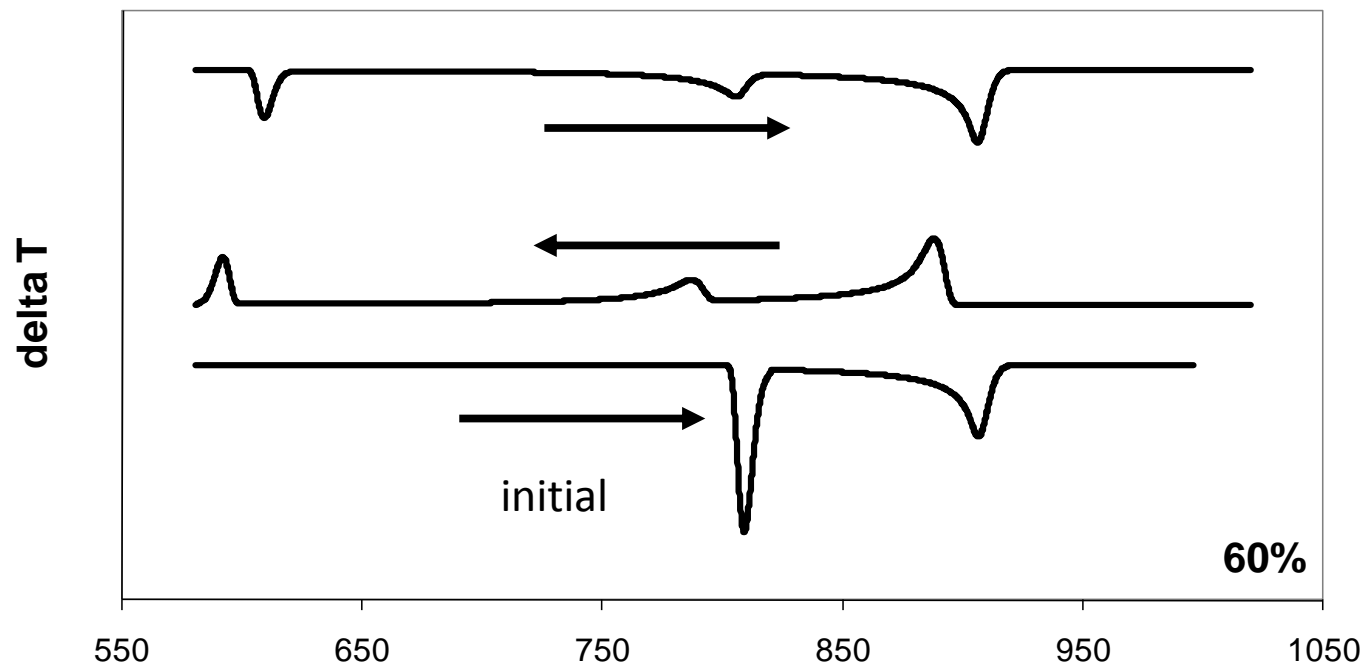
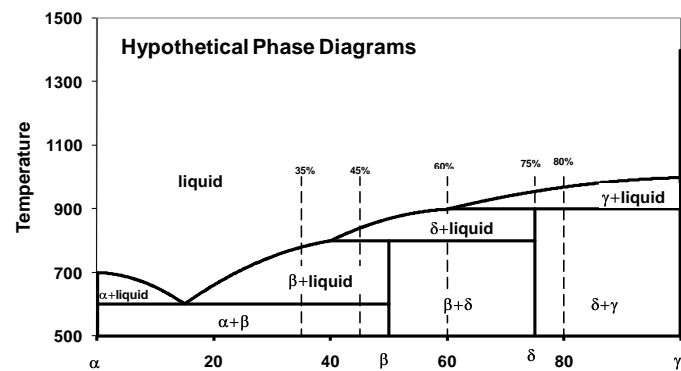


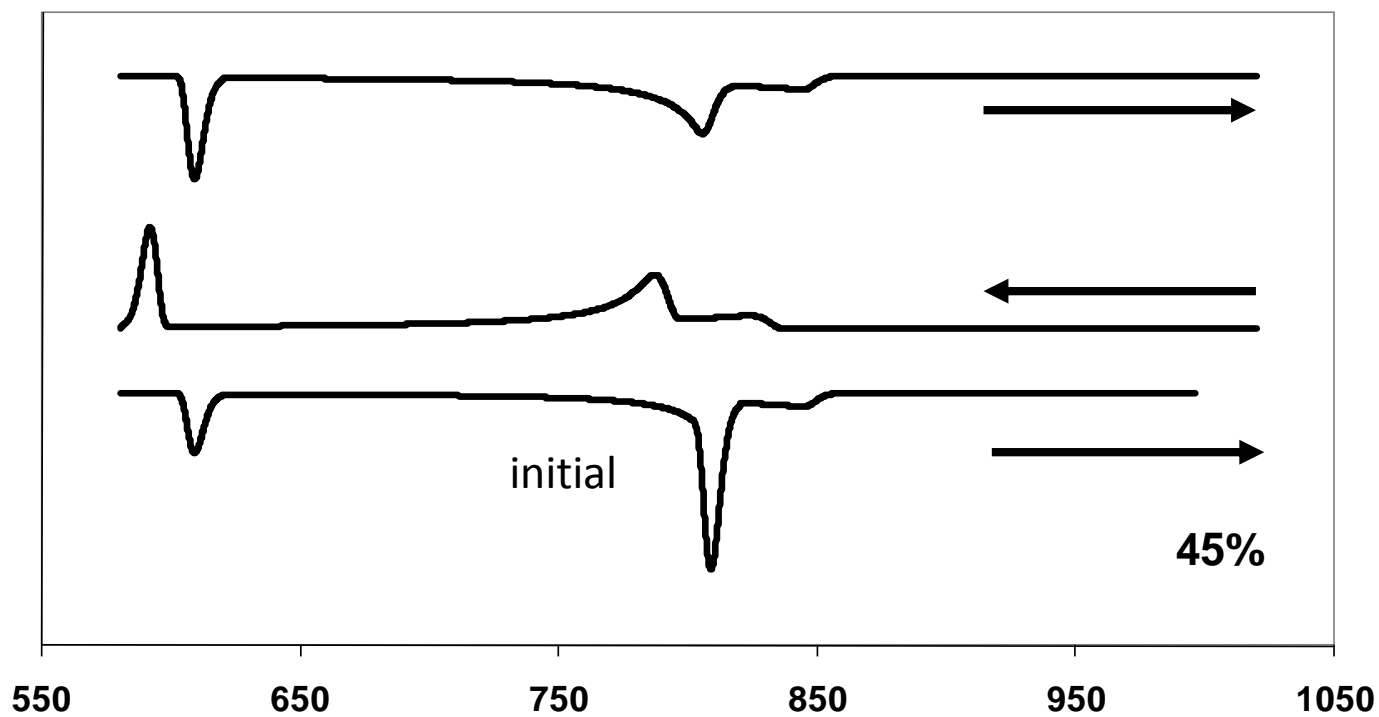
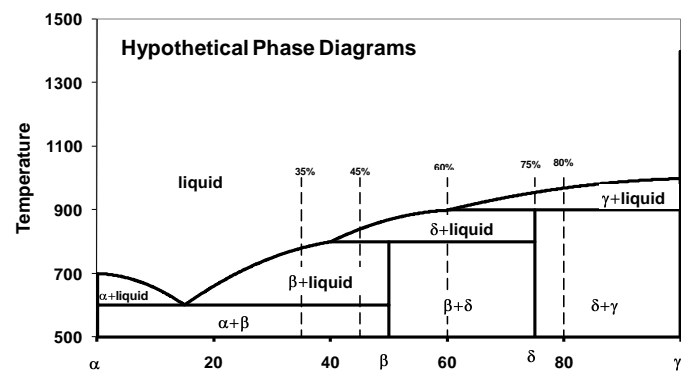


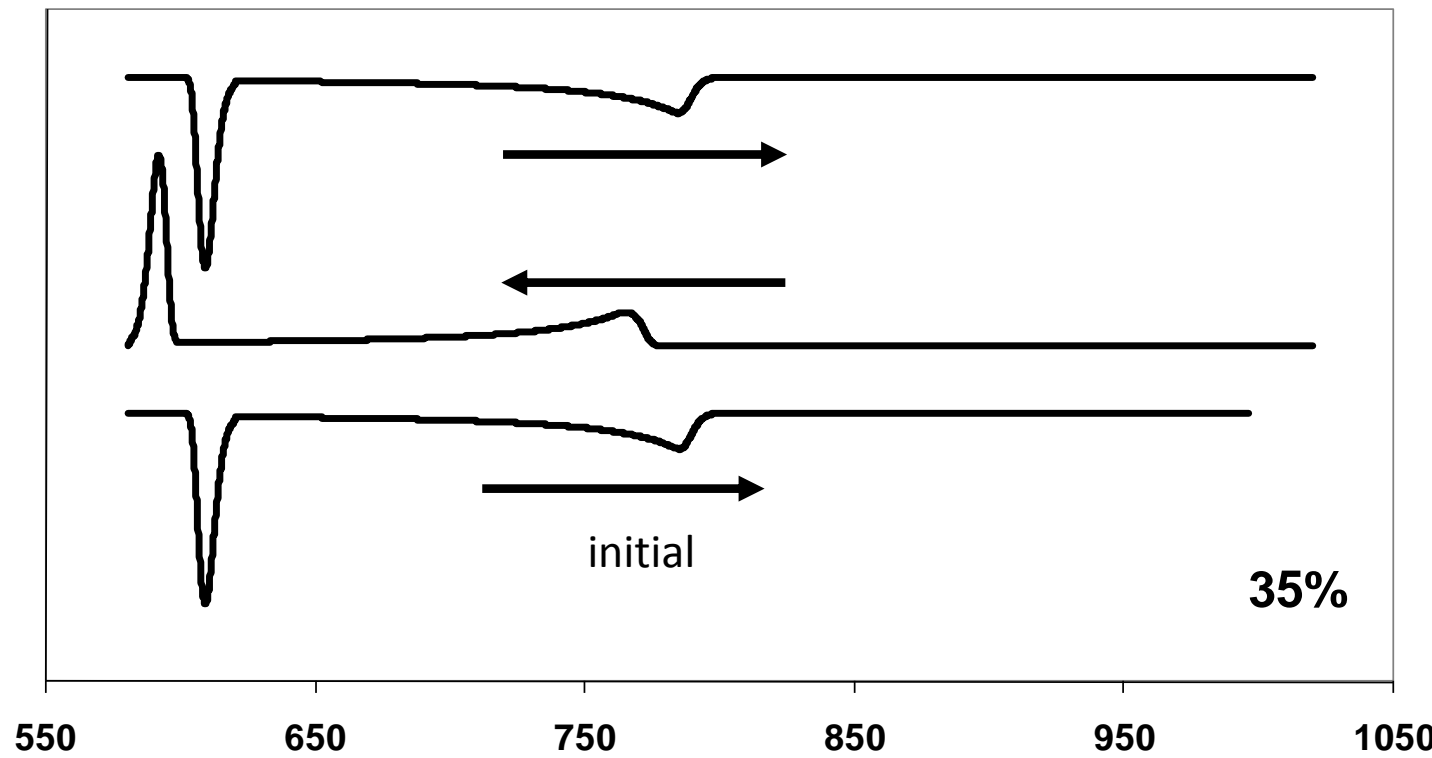
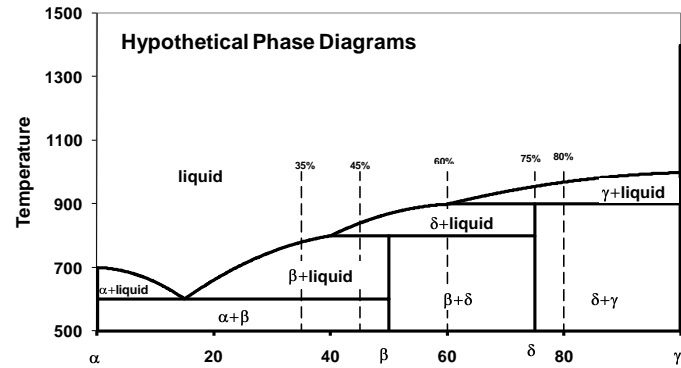
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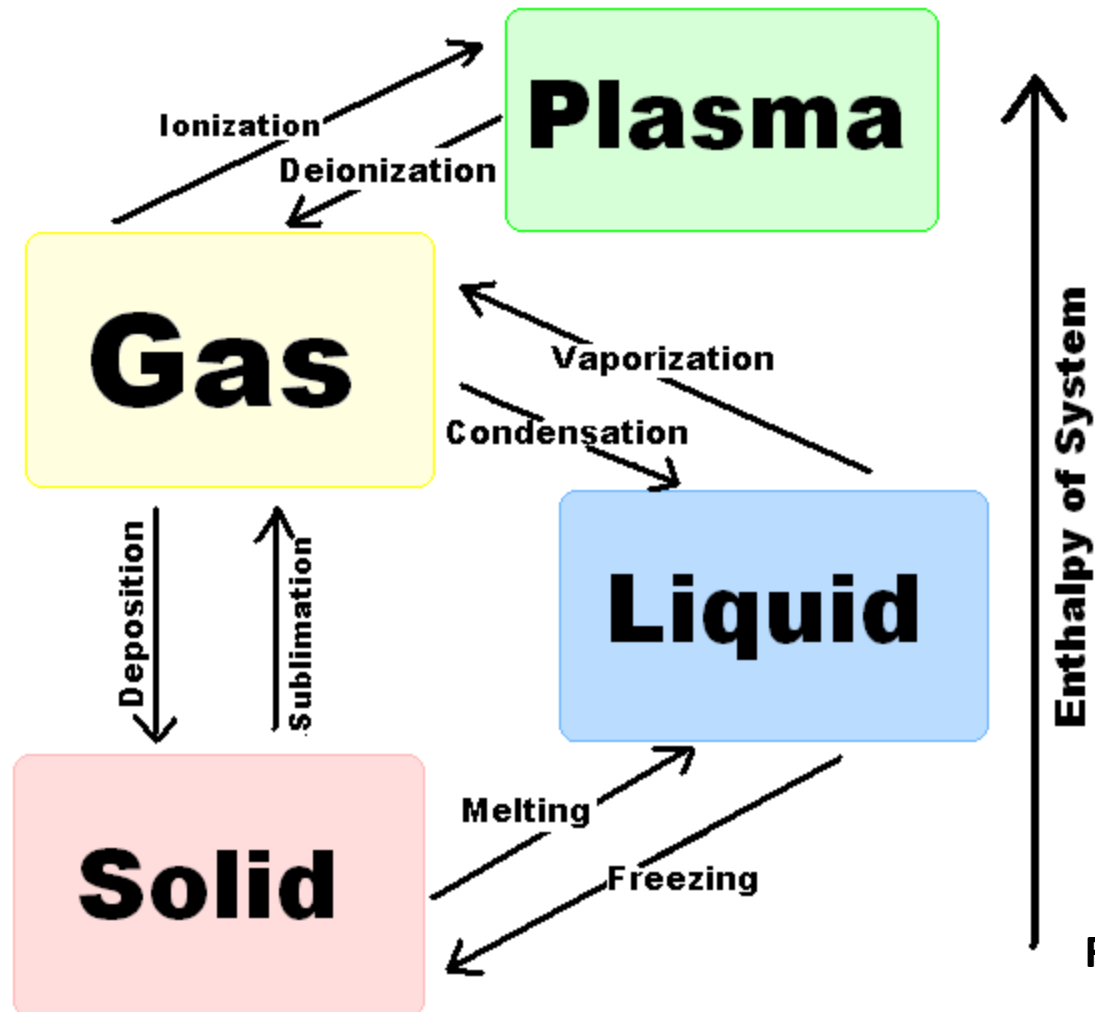








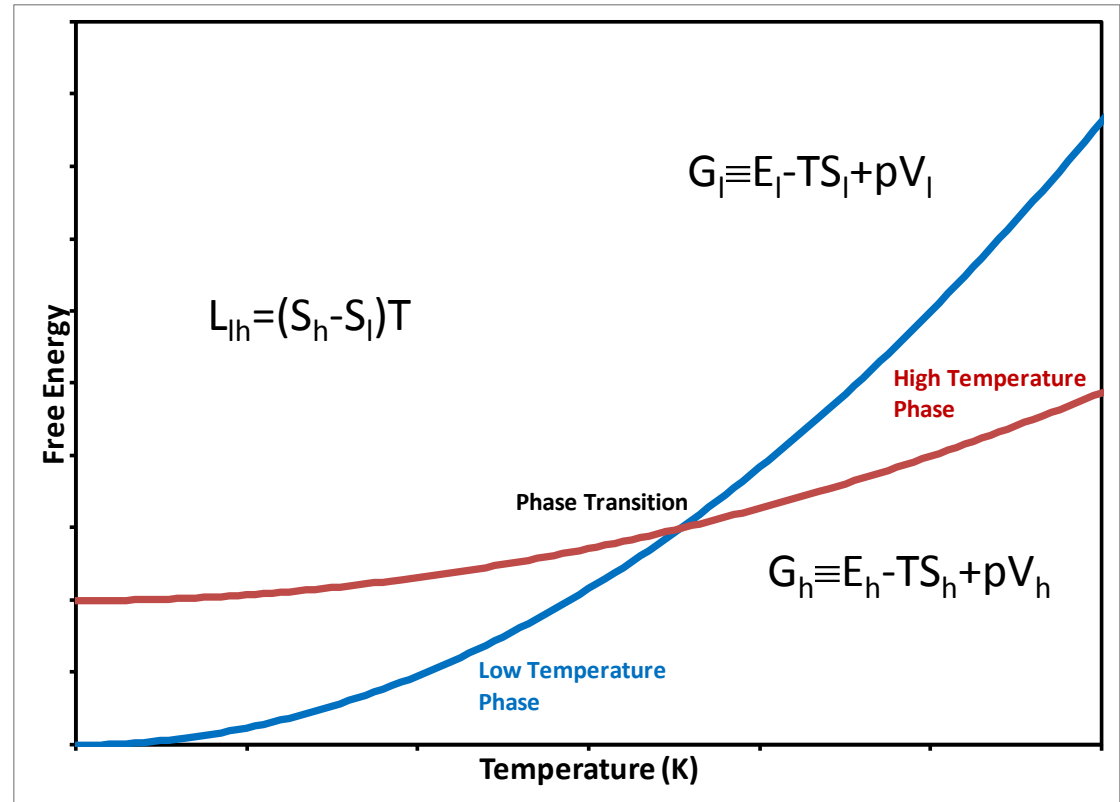
Phase transition



From Wikipedia,

Phase Transition

- At phase-transition point
 - the two phases have identical free energies
 - equally likely to exist.
- Below the phase-transition point
 - Low temperature phase is more stable state of the two.
- Above the phase-transition point
 - High temperature phase is more stable state of the two.



Types of phase transitions

- first-order phase transitions
 - involve a latent heat
 - system either absorbs or releases a fixed (and typically large) amount of energy.
 - the temperature of the system will stay constant as heat is added or released.
 - "mixed-phase regimes"
 - in which some parts of the system have completed the transition and others have not.
 - a pot of boiling water:
 - » turbulent mixture of water and water vapor bubbles.

Ehrenfest's classification of phase transitions

- phase transitions labeled by the lowest derivative of the free energy that is discontinuous at the transition.
- First-order phase transitions
 - exhibit a discontinuity in the first derivative of the free energy with a thermodynamic variable.
 - solid/liquid/gas transitions are first-order transitions
 - because they involve a discontinuous change in density (which is the first derivative of the free energy with respect to chemical potential.)
- Second-order phase transitions
 - continuous in the first derivative
 - exhibit discontinuity in a second derivative of the free energy.
 - example, the ferromagnetic phase transition in materials such as Fe,
 - **magnetization** (*the first derivative of the free energy with the applied magnetic field strength*), increases continuously from zero as the temperature is lowered below T_c
 - **magnetic susceptibility** (*the second derivative of the free energy with the field*) changes discontinuously.

International Union of Pure and Applied Chemistry.

first-order phase transition

A transition in which the molar Gibbs energies or molar Helmholtz energies of the two phases (or chemical potentials of all components in the two phases) are equal at the transition temperature, but their first derivatives with respect to temperature and pressure (for example, specific enthalpy of transition and specific volume) are discontinuous at the transition point, as for two dissimilar phases that coexist and that can be transformed into one another by a change in a field variable such as pressure, temperature, magnetic or electric field.

Example:

The transition on heating CsCl to 752 K at which it changes from the low-temperature, CsCl-type structure to the high-temperature NaCl-type structure.

Synonymous with discontinuous phase transition.

1994, 66, 583

IUPAC Compendium of Chemical Terminology 2nd Edition (1997)

second-order transition

A transition in which a crystal structure undergoes a continuous change and in which the first derivatives of the Gibbs energies (or chemical potentials) are continuous but the second derivatives with respect to temperature and pressure (i.e. [heat capacity](#), thermal expansion, compressibility) are discontinuous. Example: The [order-disorder transition](#) in metal alloys, for example, CuZn. Synonymous with [continuous transition](#).

NIST Recommended Practice Guide

Special Publication 960-15

- **DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing**
 - W. J. Boettinger, U. R. Kattner, K.-W. Moon
 - Metallurgy Division
 - Materials Science and Engineering Laboratory,
 - National Institute of Standards and Technology
 - J. H. Perepezko
 - Department of Materials Science and Engineering,
 - University of Wisconsin - Madison
 - Special Publications
 - November 2006
 - **U.S. Department of Commerce**

Terms and definitions

- ASTM E473, "Standard Terminology Relating to Thermal Analysis," is a compilation of definitions of terms used in other ASTM documents on all thermal analysis methods including techniques besides DTA and HF-DSC.
- ASTM E1142, "Terminology Relating to Thermophysical Properties," is a compilation of definitions of terms used in other ASTM documents that involve the measurement of thermophysical properties in general.

ASTM Practice Standards

- ASTM E967, "Practice for Temperature Calibration of DSC and DTA," presents simple recipes for calibration for fixed mass and heating rate using two pure materials to obtain a linear correction for conversion of measured temperature to actual temperature. The onset temperature extracted from the melting peak is determined by the extrapolation method, see section 2.4.3. For some ♦DTA and Heat-flux DSC Measurements 5 materials the standard suggests using the peak for calibration, a method not recommended for metals.
- ASTM E968, "Standard Practice for Heat Flow Calibration of DSC," uses sapphire as heat capacity standard. The method is described in section 2.4.4.
- ASTM E2253, "Standard Method for Enthalpy Measurement Validation of Differential Scanning Calorimeters," presents a method using three small masses to determine the detection limit of DTA/DSC.

ASTM Practice Standards

- ASTM E928, "Standard Test Method for Determining Purity by DSC," employs comparison of the shape of the melting peak of an impure sample to the shape for a high purity sample to determine the concentration of the impurity. The method uses the "1/F plot" which examines the down slope of the melting peak.
- ASTM E794, "Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis," employs the extrapolated onset determination method.
- ASTM E793, "Standard Test Method for Enthalpies of Fusion and Crystallization by DSC," uses area on signal vs. time plot for comparison to known heats of fusion of pure materials.
- ASTM E1269, "Standard Test Method for Determining Specific Heat Capacity by DSC," uses sapphire or aluminum as a standard.